Bulletin of Electrochemistry 12 (9) September 1996, pp 537-539

0256-1654/96/$ 3-50

TOWARDS ENERGY SAVING IN ALUMINIUM ELECTROLYSIS

UTPAL SEN

Central Electrochemical Research Institute, Karaikudi 630 006. INDIA

[Received: 14 February 1995 Accepted: 15 November 1995]

In the major aluminium producers in the world, the energy requirements for aluminium electrolysis are in the range of 14 to 15 kWh/kg of Al which is more than twice of the theoretical energy requirement for the reduction process. It is also a fact that the operational temperature of Al-electrolysis is about 1233 K which is 573 K above the melting point of Al-metal. A theoretical calculation of heat balance suggests that a reduction of about 373 K in the operational temperature of Al-electrolysis could save about 1 - 1.5 kWh/kg of Al. Another matter of concern in Al-electrolysis is the limitation of interelectrode spacing and frequent anode changing. A suitable inert anode would reduce energy losses besides saving high quality carbon uses as anode. The R & D activities undertaken by the CECRI to study such problems are discussed.

Keywords: Energy saving, aluminium and molten salt electrolysis

INTRODUCTION

The importance of Al metal for household and other purposes are well known to all of us but many may not often recall now-a-days that there was a time, not so long ago, when Al metal was more expensive than even gold. This was due to the difficulties in extraction of the metal from natural sources Only after the successful invention of Hall and Heroult which used the electrochemical route where purified aluminium oxide obtained from naturally occurring bauxite ore dissolved in the molten bath of cryolite, another naturally occurring ore, for electrolysis using carbon electrodes, Al metal was made easily available to everybody. Of course, nobody in those days had a serious thought that the demand of energy in every respect throughout the world will increase so fast and there is a definite limit of earth's energy resources which one can tap. Therefore, even though the melting point of Al metal is 933 K, the Al electrolysis was being performed at around 1273 K. This was because of the high melting point of the electrolytic bath material cryolite (~1283 K). Due to the lack of energy consciousness not much of serious efforts were reported to bring down the operating temperature of Al electrolysis even though Hall himself found out that addition of some excess AlF_3 could bring down the melting point of the cryolite bath electrolyte significantly. More than 100 years have since passed but the operational temperatures of commercial Al cells could not be brought down below 1223 K.

The energy price like in the last decade made scientists much more conscious about the necessity of bringing down the operational temperature of the Al electrolysis to get a cheaper product. A recent energy balance calculation based on the data obtained from a number of commercial Al cells throughout the world suggests that almost 50% of the energy consumed for Al metal production goes only to keep the cell body at the high operating temperatures and reduction of the operational temperature by 373 K holds the promise of saving about 1 to 1.5 kWh/kg of Al, from the heat loss alone [1].

Advantages of Al cell operation at reduced temperature

A lower cell temperature will definitely decrease the metal solubility in the bath electrolyte thereby minimising the back reaction between the dissolved metal and gas products. Obviously current efficiency will increase significantly. Lower cell temperature will also reduce the consumption of anode carbon. This will not only save precious carbon but also reduce the amount of gas evolution causing lesser air pollution in the pot room. Reduced cell operating temperature can also accrue lesser material loss by vaporization and a wider choice of materials of construction for the cells, besides providing increased pot life and improved comfort for the pot room workers.

Methods of approach for lower operating temperature

The main factors behind the high operational temperature of Al electrolysis are undoubtedly the high melting point of cryolite as bath electrolyte and low solubility of alumina in other low melting bath electrolytes. The efforts to bring down the operational temperature are consequently based on the following three possible approaches.

1. The first approach is the replacement of both cryolite as bath electrolyte and alumina as the cell feed for electrolysis. Normally chloride salts have lower melting points than the corresponding fluorides. So the chloride route of electrolysis may be the answer. In this approach the raw material alumina is to be chlorinated to form $AlCl_3$ which is then to be dissolved in any suitable mixed chloride salt bath of low melting point for electrolysis. A few years ago considerable efforts were put to develop such a process [2]. However, this method never became popular presumably because of the difficulties in handling the highly hygroscopic and volatile raw material $AlCl_3$. Besides, an additional step was also involved to prepare $AlCl_3$ from purified alumina.

2. The second approach is not only the replacement of cryolite bath but use of alumina as the raw material as well as the cell feed. This method is still in an early stage of development and is essentially based on the preparation of composite anodes of suitable compositions consisting of alumina and carbon and effective consumption of such anodes by electrolysis in a low melting fluoride-chloride bath electrolyte to produce Al metal [3-4]. The anticipated major problems of this method are carbon contamination and sludge formation. This method would also need modification in cell design.

3. The third approach which presently attracts most attention from the scientists is to retain both cryolite and alumina by introducing new additives. The idea is to find out some suitable additives to the cryolite bath which will decrease the liquid temperature considerably without affecting the alumina solubility in the bath and its electrical conductivity [5].

Research work undertaken by the CECRI

Composite anodes

The Electropyrometallurgy Division of the CECRI is involved in the laboratory experiments for the development of consumable composite anodes for Al electrolysis. We have fabricated some composite anode blocks consisting of carbon and alumina, characterized them and operated a 50 A capacity Al cell with some success [4]. We are able to get the anode consumed at a reasonable rate and make the alumina present in the anode available for the reduction and obtained Al metal as the electrolysis product. The operating data of such experimental cell are listed in Table I. Further work is however necessary for developing the process.

Low melting cryolite bath for Al electrolysis

The choice of additives, which will serve the dual purpose of decreasing the liquids temperature of the bath and at the same time, will not reduce the electrical conductivity of the modified bath, is extremely limited. No doubt the addition AlF_3 can sharply reduce the melting point of cryolite but at the same time the bath conductivity will also decrease sharply [6]. Presently the most common additives to the cryolite bath being tried by the scientists are limited to CaF_2, MgF_2 and LiF (often added as Li_2CO_3) besides, of course, AlF_3 and the mixture of some or all of them. AlF_3, CaF_2 and MgF_2 decrease the liquid temperature of the cryolite bath and reduce the metal solubility in it, but due to the simultaneous decrease of alumina solubility and the bath conductivity they are not very attractive even though they are occasionally used in small quantities to bring some small benefits [7] LiF which can be introduced by adding Li_2CO_3, on the other hand, increases the bath conductivity at the same time decreasing the liquids temperature. But the high cost of making up of its loss during cell operations does not seem to make its use economical [8].

We have developed some effective additives from the mixtures of fluorides and chlorides of aluminium, calcium and sodium which provide a sharp decrease in the liquids temperature, at the same time maintaining the alumina solubility and the bath conductivity to the original level. We have operated a number of 500 A capacity Al cells at 1093 K employing the electrolyte bath with the newly developed additive mixture. The operational data are given in Table II.

Continuous operations of some higher capacity Al cells at 1093 K are necessary for obtaining reliable data regarding current efficiency, vaporization loss of the electrolyte or its components. Flue gas analysis is also to be done for confirming the electrolysis products. Besides, a number of basic studies are to be conducted to develop the best possible combination for the bath electrolyte for low temperature Al

TABLE I: Operating data of aluminium electrolysis with composite anodes

1. Capacity of Al cell	50 A
2. Bath electrolyte	(1:1) NaF + KCl mixture
3. Cathode	Graphite
4. Anode	Composite of carbon and alumina
5. Anode, cathode spacing	1.5 cm
6. Operating temperature	923 K
7. Cell voltage	4.0 V
8. Anode current density	0.6 A/cm^2
9. Anode efficiency	97%
10. Cathodic efficiency	70%
11. Duration of operation	2 days

electrolysis. We believe that there is a tremendous possibility for success in bringing down the operational temperature of Hall-Herout Al cell by introducing effective additives.

Inert anodes

Most of the commercial plants for Al electrolysis achieved current efficiencies well above 90% which is usually equivalent to the energy consumption at around 14 kWh/kg of Al. But the energy efficiency remains well below 50% of the theoretical value. Although low temperature cell operation would push the current efficiency further close to 100%, further improvement in the energy efficiency will require radical changes in cell design and electrode materials. The cell voltages employed in most of the commercial Al cells are in the range of 4.2 - 4.5 even though the theoretical reversible potential of the reduction process along with the over voltages in carbon electrodes amounts to only 2V. According to some calculation the busbar connection resistance and the internal electrolyte resistance (IR drop) amount to 20% and 40% of the employed cell voltage, respectively [2]. Such a high internal resistance is due to the interelectrode spacing which is restricted to not less than 4.5 cm [9]. The electromagnetic wave formation in the electrode which is being continuously consumed are responsible for such limitations. To reduce the IR drop in Al electrolysis inert electrode materials must be developed and at present it is the belief of the scientists that the replacement of the carbon anode by mixed oxide anodes and introducing TiB_2 cathode material may be the answer to this problem [10,11]. Apart from that the replacement of carbon anodes by insert anodes would save about 500 kg of carbon per ton of Al metal produced. Ferrities of nickel and cobalt are among the most common mixed oxides which are being worked upon. The major problems encountered with the inert anodes are (a) corrosion of the anode, (b) contamination of the metal, and (c) contact problems, cracking, etc.

TABLE II: Operating data of low temperature aluminium electrolysis

1. Capacity of the cell	450 A
2. Electrolyte	Cryolite+(0-10%) additive
3. Operational temperature	1093 K
4. Bath conductivity at 1093K	2.5 $ohm^{-1}\ cm^{-1}$
5. Alumina solubility at 1093 K9%	
6. Anode	Graphite
7. Anode cathode spacing	5 cm
8. Cell voltage	5 V
9. Anode current density	1 A/cm^2
10. Cathode current density	0.5 A/cm^2
11. Alumina concentration in the bath	6 to 7%
12. Alumina feeding	once in 30 minutes
13. Current efficiency	80%
14. Carbon consumption	0.6 kg/kg of Al
15. Purity of metal produced	
Aluminium	99.40%
Fe	0.47%
Si	0.17%
Na	0.0025%

TABLE III: Important properties of ferrites

Samples	T K	Density g/cm^3	Porosity %	Hardness VPN	Ele. Cond Mhos
	305	3.3	41	—	10^{-5}
$CoFe_2O_4$	1273	4.0	21	480	3.4
	1623	5.0	9	580	6.0
	305	3.4	42	—	10^{-8}
$NiFe_2O_4$	1273	4.0	19	450	1.5
	1623	4.8	11	540	2.5

Research efforts in the CECRI to develop inert anodes

We are able to fabricate inert anodes with mixed oxides of ferrite of nickel and cobalt with additions of rare earth oxides by high pressure compacting of power blend in the required composition. Green compacts were than sintered at high temperatures of upto 1773 K. The sintered pellets were then subjected to detailed characterization for assessing their physical, chemical and structural properties by various methods. It has been found that the pellets are mechanically strong. Table III shows some of the properties [12]. These pellets will be tested in small lab scale Al cells.

REFERENCES

1. Qiu Thaxian, *Light Metals,* **591** (1988)
2. J Thonstad, *Advances in Molten Salt Chemistry,* Vol 6, (eds) G Mamantov, C B Mamantov and J Braunstein, Elsevier, New York, **2** (1987) 73
3. A P Ratvik, T M Laher, G Mamantov, S S Roberts and J Y Josefwiez, *J Electrochem Soc,* **134** (1987) 321
4. J N Balaraju, V Ananth and U Sen, *J Electrochem Soc,* Vol 142, (**2**) (1995) 439
5. W Hauopin, *J Metals,* **43(11)** (1991) 28
6. K Grjotheim, C Krohn, M Malinovsky and J Thonstad, *Aluminium electrolysis,* 2nd edition, Aluminium Verlag, Dusseldrof, Germany (1982)
7. K Grjothim, H Kvande and B J Welch, *Light Metals,* **417** (1988)
8. R D Peterson and T Tabereaux, *Light Metals,* **647** (1988)
9. N Jarrett, *Production of aluminium and alumina,* A R Burkin, John Wiley and Sons, Chichester, **13** (1987) 188
10. T R Alcom, A T Tabereaux, N E Richards, C F Windisch, Jr D M Strachan, J S Gregg and M S Frederick, *Light Metals,* **433** (1993)
11. W Huazhand, L Yexiang, W Huiling and Xianguin, *Light Metals,* **505** (1994)
12. C O Augustin and P S Desikan, *Proceedings 2nd International conf on Aluminium,* INCAL 91, AAI, Bangalore, 345